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Easily Vaporizable Ionic Liquids – No Contradiction!

Martin Köckerling,*[a] Tim Peppel,[b] Philipp Thiele,[a] Sergey P. Verevkin,*[c] Vladimir N. Emel'yanenko,[d] Artemiy A. Samarov,[e] and Wolfgang Ruth[f]

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It was a big surprise to see crystals of an ionic liquid (IL) forming by sublimation at room temperature. ILs are generally accepted to have negligible vapour pressures at elevated temperatures, making their sublimation or distillation very difficult. ILs that sublime easily contain silylimidazolium-based cations. In order to establish the details of the unusual behaviour of this subclass of ILs, a combined spectroscopic, X-ray crystallographic, physicochemical and theoretical characterization was performed. The results are compared with those of other easily vaporizable compounds, like ammonium chloride and naphthalene. The single-crystal X-ray structure analysis of one of these compounds, *N*-methyl-*N*′-dimethyl(phenyl)silylimidazolium chloride (monoclinic, *C*2/*c*), clearly shows the existence of isolated ions, demonstrating that the compound is an ionic liquid.

Introduction

Ionic liquids (ILs) have been receiving much attention in the last decade from both industrial and academic researchers.[1–3] ILs are salts with melting points below 100 °C. They can exhibit intrinsically useful properties, such as wide liquid ranges (up to 400 °C), negligible vapour pressures, large electrochemical windows and high electric conductivities.[4] Such compounds are being applied as solvents for chemical processes,[5–7] liquid–liquid extractions,[8] electrodeposition[9,10] and spectroscopic studies,[9–15] as electrolytes in solar cells[16,17] and as components in hybrid materials.[18] One of the unique features of ILs is the tuneability of their chemical and physical properties by selection of an appropriate anion/cation combination.

The claim that easily vaporizable ILs exist sounds implausible, because previous data clearly show that ILs usually exhibit negligible vapour pressures at room temperature.[19,20] Nevertheless, some ILs can be vaporized and distilled, but only under high vacuum and at high temperatures.[21–26]

In this paper we present results of investigations on ILs containing silylimidazolium cations (SILs), which sublime easily at room temperature.

Results and Discussion

It was a very surprising observation in the laboratory that within a day under approximately normal conditions large amounts of crystals of ILs containing silylimidazolium-based cations (SILs) formed under the lid of the storage vessel – the substances may only have reached the top of the vessel only via the gas phase (see Figure 1).

Spectroscopic and powder-XRD measurements undoubtedly show that the composition and structures of the four ILs containing silylimidazolium cations, *N*-methyl-*N*′-trimethylsilylimidazolium bromide (**1**; MTMSIm-Br), bis(*N*,*N*′-trimethylsilyl)imidazolium bromide (**2**; BTMSIm-Br), *N*-methyl-*N*′-trimethylsilylimidazolium chloride (**3**; MTMSIm-Cl) and *N*-methyl-*N*′-dimethyl(phenyl)silylimidazolium chloride (**4**; MDMPhSIm-Cl), before and after sublimation are identical. A complete single-crystal X-ray determination of the structure of MDMPhSIm-Cl (Figure 2) shows that indeed noncovalently bonded Cl^- anions and isolated silylimidazolium cations are present, as expected components of ILs.

How can we explain this unexpected behaviour of easy sublimation for this subclass of ILs? A probable explanation can be found by comparison with the sublimation of ammonium chloride (NH_4Cl). NH_4Cl can be sublimed in the temperature range 80–100 °C at ambient pressure or at

[a] Institut für Chemie, Anorganische Festkörperchemie, Universität Rostock, Albert-Einstein Str. 3a, 18059 Rostock, Germany
E-mail: Martin.Koeckerling@uni-rostock.de
http://www.koeckerling.chemie.uni-rostock.de/
[b] Leibniz Institut für Katalyse e.V. an der Universität Rostock, Anorganische Funktionsmaterialien, Albert-Einstein-Str. 29a, 18059 Rostock, Germany
[c] Institut für Chemie, Physikalische Chemie, Universität Rostock, Dr.-Lorenz-Weg 1, 18059 Rostock, Germany
[d] Department of Physical Chemistry, Kazan Federal University, Kremleskaya Str. 18, 420008 Kazan, Russia
[e] Department of Chemical Thermodynamics and Kinetics, St. Petersburg State University, Universitetskiy Prospect 26-Peterhof, 198504 Saint-Petersburg, Russia
[f] Institut für Chemie, Technische Chemie, Universität Rostock, Albert-Einstein Str. 3a, 18059 Rostock, Germany
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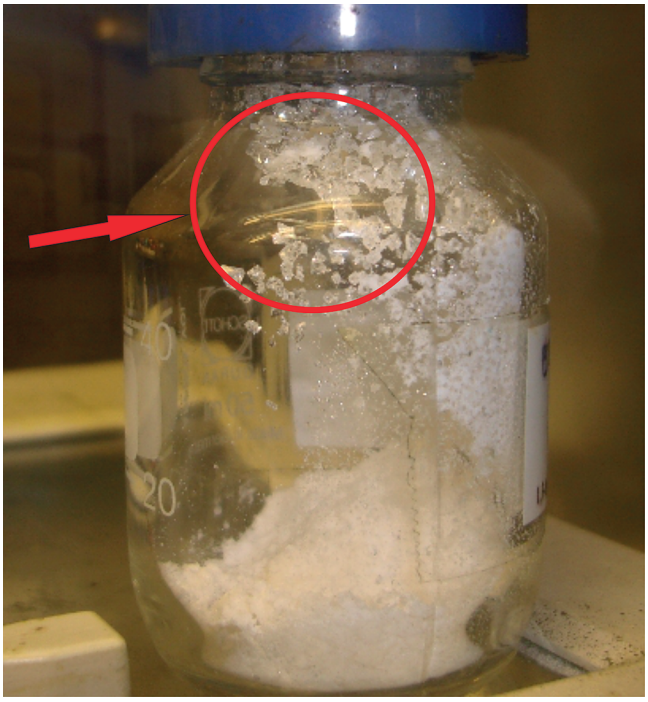

Figure 1. Crystals of an IL with silylimidazolium cations, obtained by sublimation.

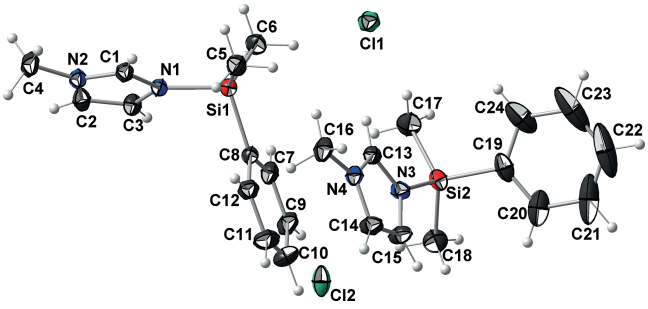

Figure 2. Structure of the two symmetrically independent ion pairs in crystals of MDMPhSIm-Cl (thermal ellipsoids at 50% probability at 173 K).

room temperature in vacuo. The mechanism of sublimation for this salt is known. It is proven that NH_4Cl dissociates in the gas phase into NH_3 and HCl by proton transfer and the two components react again under cooling to yield NH_4Cl.[27] Such proton transfer mechanisms have been shown to occur also in acidic ILs.[28] The main question is whether this behaviour of dissociation and association can be transferred to the behaviour of SILs. First hints are given by NMR spectroscopic investigations in solution. It has been shown that solutions of SILs consist of undecomposed SILs and their dissociation products.[29] In order to obtain a detailed answer to the question whether the behaviour in solution can be applied to that in the gas phase, three different methods can be used: (1) thermochemical measurements of the enthalpies of sublimation of the SILs (quantitative analysis), (2) determination of the gas composition above the solid/liquid SILs (e.g. by GC/MS analysis) and (3) theoretical investigations of thermodynamic parameters by using quantum chemical methods. In this publication we report the results of investigations by all three methods in detail.

Temperature-dependent thermodynamic parameters, that is vapour pressure and the derived molar enthalpy of sublimation, $\Delta_{sub}H_m$, have been measured for MTMSIm-Br (**1**) and BTMSIm-Br (**2**) by applying the transpiration method.[30] Additional data for the enthalpies of sublimation have been established by thermogravimetric analysis (TGA)[31] (for experimental details, see the Supporting Information). The measured data, adjusted to the reference temperature 298 K, are compiled in Table 1 with some literature values for comparison.

Table 1. Experimental thermodynamic data of SILs **1** and **2** and (BMIm)[$N(CN)_2$] and NH_4Cl, adjusted to 298 K.

Compound[a]	Method[b]	$\Delta_{sub}H_m$ [kJ/mol]	T_{melt} [K]
1	T	99 ± 2	495
	TGA	100 ± 3	
2	T	109 ± 3	442
	TGA	112 ± 1	
BMIm[$N(CN)_2$]	T	157 ± 1[c] [19]	–
NH_4Cl	Ef	89.1 ± 0.1[32]	793

[a] Because of its strong hygroscopic behaviour, no reliable data exist for MTMSMIm-Cl (**3**). [b] T: transpiration; TGA: thermogravimetry; Ef: Knudsen effusion. [c] Enthalpy of vaporization.

From Table 1, it is obvious that the sublimation enthalpies measured by two independent methods are in agreement within experimental error. Surprisingly, they are far below (ca. 65%) the enthalpies of sublimation or vaporization of other conventional ILs that have nearly the same molar mass {e.g. (BMIm)[$N(CN)_2$]} and fall within the range of values for NH_4Cl. The same conclusions are valid, if the average, T_{av}, of the measurements is used (see the Supporting Information). Enthalpies of melting are also known for T_{av} from DSC measurements, and hence it is possible to derive enthalpies of vaporization, $\Delta_{vap}H_m$. Surprisingly, $\Delta_{vap}H_m$ for BTMSIm-Br (**2**) equals 47.6 kJ/mol (T_{av} = 406 K), and this value is slightly above the $\Delta_{vap}H_m$ value for water (44 kJ/mol).[33]

What is the mechanism of sublimation that is in accordance with the astonishingly low enthalpies of sublimation, $\Delta_{sub}H_m$, for SILs? The process of sublimation for NH_4Cl is well characterized, and it is known that neutral molecules of NH_3 and HCl are present in the gaseous state, which react to yield NH_4Cl upon condensation.[34,35] In this work, we estimated the equilibrium constant for the dissociation reaction [Equation (1)] by means of the G3MP2 method; K_p = 24.6 (T = 393 K).

$$NH_4Cl \rightarrow NH_3 + HCl \quad (1)$$

This value clearly indicates that NH_4Cl is completely dissociated in the gaseous state and that dissociation is favoured over sublimation of ions. This is made possible by proton transfer. Proton transfer is impossible for the SILs

investigated in this paper; hence (at least) two scenarios are conceivable: (1) dissociation of the solid SILs with sublimation into the molecular starting compounds, which are able to react back to the SILs upon cooling (see NH_4Cl), or (2) dissociation of the SILs into cations and anions upon transfer into the gaseous state. In order to find out which species are present in the gaseous state, thermodynamic parameters Δ_rG^0, Δ_rH^0, Δ_rS^0 and K_p, were obtained by means of the CBS–QB3 composite method.[36] The values for the hypothetical sublimation processes [Equations (2), (3), (4) and (5); (X = Cl, Br)] were estimated. Results for 298 K and 403 K are summarized in Tables 2 and 3, respectively.

$$\text{MTMSIm-X} \rightarrow \text{TMS-X} + \text{MIm} \rightarrow \text{MTMSIm-X} \quad (2)$$

$$\text{BTMSIm-X} \rightarrow \text{TMS-X} + \text{TMSIm} \rightarrow \text{BTMSIm-X} \quad (3)$$

$$\text{MTMSIm-X} \rightarrow \text{MTMSIm}^+ + \text{X}^- \rightarrow \text{MTMSIm-X} \quad (4)$$

$$\text{BTMSIm-X} \rightarrow \text{BTMSIm}^+ + \text{X}^- \rightarrow \text{BTMSIm-X} \quad (5)$$

Table 2. Thermodynamic data for Equations (2) and (3) obtained by CBS–QB3 calculations.

298 K	Equation (2)		Equation (3)	
Parameter	X = Cl	X = Br	X = Cl	X = Br
$\Delta_rG°$ [kJ/mol]	–77.6	–41.9	–60.5	–24.0
$\Delta_rH°$ [kJ/mol]	–30.9	2.2	–16.9	19.0
$\Delta_rS°$ [J/mol K]	156.7	147.9	146.2	144.4
K_p	4.0×10^{13}	2.2×10^{7}	3.9×10^{10}	1.6×10^{4}
403 K	Equation (2)		Equation (3)	
Parameter	X = Cl	X = Br	X = Cl	X = Br
$\Delta_rG°$ [kJ/mol]	–45.1	–15.4	–75.5	–
$\Delta_rH°$ [kJ/mol]	7.8	38.5	–18.9	–
$\Delta_rS°$ [J/mol K]	131.2	133.8	140.4	–
K_p	7.0×10^{5}	1×10^{2}	6.1×10^{9}	–

Table 3. Thermodynamic data for Equations (4) and (5) obtained by CBS–QB3 calculations for X = Br (T = 298 K).

Parameter	Equation (4)	Equation (5)
$\Delta_rG°$ [kJ/mol]	363.3	360.7
$\Delta_rH°$ [kJ/mol]	383.2	386.8
$\Delta_rS°$ [J/mol K]	66.8	90.2
K_p	2×10^{-64}	8×10^{-64}

Dissociation of SILs as shown in Equations (4) and (5) can be virtually excluded, because of the very small equilibrium constants (magnitude 10^{-64}). In contrast, the K_p values for Equation (2) clearly show that the SILs are present as molecular, uncharged starting materials in the gaseous state [298 K, Br species: $K_p = 2.2\times10^7$ and $K_p = 1.6\times10^4$ for Equation (3); see Table 2]. At 403 K, the equilibrium constants are significantly smaller, but they still have a magnitude that indicates a preference of neutral molecules over charged ions in the gaseous state. Exclusively two mass peaks of SILs can be detected in GC–MS measurements, which belong to trimethylsilyl halides and substituted imidazoles. The fact that SILs dissociate into neutral starting molecules under sublimation conditions seems at first glance contradictory with the fact that SILs can be obtained in high yield by the reaction of the starting materials. However, the synthesis is performed in solution, and to clarify that this is no contradiction, the K_p for the reaction given in Equation (2) (X = Br) was converted into K_a for the liquid phase [Equation (6)].

$$K_a = K_p[P_{SIL}/(P_{MIm}P_{TMSBr})] \quad (6)$$

In this equation, P_{SIL}, P_{MIm} and P_{TMSBr} are the vapour pressure values of the species participating in the reaction. The vapour pressures of the precursors are known from the literature,[37–39] and for P_{SIL} the value for (BMIm)[$N(CN)_2$] was used, because of its comparable molar mass.[19] The calculated value at 298 K is as follows: $K_a = 3.6\times10^{-9}$ for the dissociation of MTMSIm-Br according to Equation (2) in the liquid phase and $K_a = 1/(3.6\times10^{-9}) = 2.8\times10^8$ for the formation of SIL. This value indicates that the equilibrium in the liquid phase is (almost) completely on the side of SIL formation. The values for the gaseous and the liquid phase are therefore in accordance with the experimental findings, and the inaccuracies of the vapour pressures values used become irrelevant. At this point, it is interesting to compare the unusual behaviour of these ILs with that of other easily vaporizable solids. For this comparison, thermodynamic data of ionic compounds are compiled in Table 4 and those of molecular organic solids in Table 5.

The thermodynamic function that takes enthalpy and entropy factors for the sublimation process into account is the Gibbs energy, $\Delta_{sub}G_m$. For the investigated SILs, the values range from 20 to 30 kJ/mol. The value for the easily vaporizable NH_4Cl (22.0 kJ/mol) is found within this range, whereas the value for the difficult to vaporize IL (BMIm)[$N(CN)_2$] is larger by a factor of about 2 to 3. Therefore, the Gibbs energy is a reliable quantitative function to describe the sublimation behaviour of the title SILs. In addition, the $\Delta_{sub}G_m$ value for naphthalene (see Table 6), which is also one of the compounds that easily disappear from the lab bench, is found in this same range. Accordingly, naphthalene, ammonium chloride and MTMSIm-Br have similar values for the Gibbs energy; they all have high volatility but have different mechanisms for the sublimation process.

The remarkably easy sublimation of Si-containing ILs could lead to industrial applications. Using SILs as solvents could be an elegant method, for example for the preparation of nanoparticles, because the particles could easily be separated from the solvent by evaporation.

Table 4. Thermodynamic data for solid ionic compounds at T = 298 K.

Parameter	MTMSIm-Br[a]	BTMSIm-Br[a]	NH_4Cl[a]	(BMIm)[$N(CN)_2$][b]
$\Delta_{sub}H_m$ [kJ/mol]	98.9 ± 2.0	109.64 ± 3.0	89.1 ± 0.1	157.2 ± 1.2
$\Delta_{sub}S_m$ [J/mol K]	178.1 ± 6.8	164.4 ± 10.1	151.6 ± 0.4	248.2 ± 4.2
$\Delta_{sub}G_m$ [kJ/mol]	22.9	30.3	22.0	83.2
P_{298} [Pa]	1×10^{-3}	2×10^{-6}	2×10^{-3}	3×10^{-10}

[a] These data are referenced to the sublimation process. [b] These data are referenced to the vaporization process. The experimental data (see the Supporting Information), are adjusted to the reference temperature of T = 298 K by using $\Delta_{sub}C_p$ = –40 J/(mol K) for MTMSIm-Br and $\Delta_{sub}C_p$ = –60 J/(mol K) for BTMSIm-Br.

Table 5. Thermodynamic data for solid molecular compounds at T = 298 K.

Parameter	Benzene[40]	Naphthalene[41]	Biphenyl[42]	Anthracene[43]
$\Delta_{sub}H_m$ [kJ/mol]	45.5 ± 0.5	73.0 ± 0.2	83.7 ± 0.4	98.8 ± 0.6
$\Delta_{sub}S_m$ [J/mol K]	176.4 ± 1.1	169.0 ± 0.7	187.1 ± 1.3	179.2 ± 2.1
$\Delta_{sub}G_m$ [kJ/mol]	–7.1	22.6	27.9	45.3
P_{298} [Pa]	2×10^6	10.9	1.3	1×10^{-3}

Table 6. Crystal data, structure solution and refinement parameters for MDMPhSIm-Cl.

Formula	$C_{12}H_{17}ClN_2Si{\cdot}0.25(C_3H_4N_2)$
Fw [g/mol]	269.84
Space group	$C2/c$
a [Å]	43.922(1)
b [Å]	7.8460(2)
c [Å]	17.9152(5)
α [°]	90
β [°]	107.000(2)
γ [°]	90
V [Å^3]	5904.1(3)
Z	16
$2\theta_{max}$ [°]	72.34
T [K]	173(2)
Reflections collected	75059
Unique reflections	14014
R_{int}	0.0585
Parameters refined	519
$R1/wR2$ [$I > 2\sigma(I)$]	0.0444/0.1218
$R1/wR2$ (all data)	0.0663/0.1384
GOF	1.019

Conclusions

ILs with imidazolium-based cations, which contain N-bonded silylorganic groups, were synthesized. They have the unexpected property of easy vaporization. Physicochemical and theoretical investigations established the mechanism of vaporization. On vaporization, neutral molecules are formed from the charged ions of these ILs. The Gibbs energy for the sublimation process, accessible through quantum chemical calculations, has been shown to predict the thermal behaviour quite well.

Experimental Section

Materials and Procedures: *N*-Methylimidazole and bromotrimethylsilane were purchased from Sigma–Aldrich (> 99%) and freshly distilled prior to use. *N*-trimethylsilylimidazole was synthesized according to a known literature method.[44] All experimental procedures were performed under strict exclusion of moisture, that is, by using Schlenk techniques or glove boxes.

***N*-Methyl-*N*′-trimethylsilylimidazolium Bromide (1; MTMSIm-Br):**[45] *N*-Methylimidazole (17.9 g, 0.2 mol) was slowly added dropwise to a solution of bromotrimethylsilane (33.4 g, 0.2 mol) in dry diethyl ether (100 mL) under Ar at 0 °C. The resulting white precipitate was filtered off washed thoroughly with diethyl ether and finally dried in vacuo at ambient temperature. MTMSIm-Br was stored in a screw-cap vessel in an Ar-filled glove box at ambient temperature, which resulted in the sublimation of the powder and appearance of colourless crystals at the bottom of the screw cap. Yield: 45.0 g (88%). M.p. 115 °C (decomp.). No satisfactory elemental analysis results were obtained for $C_7H_{15}BrN_2Si$ because of the highly reactive nature of the compound. ^{1}H NMR ($CDCl_3$): δ = 0.64 (s, 9 H, Si–Me_3), 4.12 (s, 3 H, N–Me), 7.28 (s, 1 H, N–CH–CH–N), 7.51 (s, 1 H, N–CH–CH–N), 9.86 (s, 1 H, N–CH–N) ppm. ^{13}C NMR ($CDCl_3$): δ = –0.5 (Si–Me_3), 36.5 (N–Me), 122.8 (N–CH–CH–N), 124.2 (N–CH–CH–N), 139.6 (N–CH–N) ppm.

Bis(*N*,*N*′-trimethylsilyl)imidazolium Bromide (2; BTMSIm-Br):[29] Bromotrimethylsilane (5.5 g, 35.7 mmol) was slowly added dropwise to a solution of *N*-trimethylsilylimidazole (5.0 g, 35.7 mmol) in dry *n*-hexane (100 mL) under Ar at ambient temperature. The resulting white precipitate was filtered off, washed thoroughly with *n*-hexane and diethyl ether and finally dried in vacuo at ambient temperature. BTMSIm-Br was stored in a screw-cap vessel in an Ar-filled glove box at ambient temperature, which resulted in the slow sublimation of the powder and appearance of colourless crystals at the bottom of the screw cap. Yield: 7.0 g (67%). M.p. > 80 °C (decomp.). No satisfactory elemental analysis results were obtained for $C_9H_{21}BrN_2Si_2$ because of the highly reactive nature of the compound. ^{1}H NMR (CD_3CN): δ = 0.61 (s, 9 H, Si–Me_3), 7.57 (s, 2 H, N–CH–CH–N), 8.88 (s, 1 H, N–CH–N) ppm. ^{13}C NMR (CD_3CN): δ = –0.8 (Si–Me_3), 125.3 (N–CH–CH–N), 143.6 (N–CH–N) ppm. ^{29}Si NMR (CD_3CN): δ = 31.2 ppm.

***N*-Methyl-*N*′-trimethylsilylimidazolium Chloride (3; MTMSIm-Cl):**[46] Freshly distilled *N*-methylimidazole (8.21 g, 0.1 mol) was combined at room temperature with chlorotrimethylsilane (10.86 g, 0.1 mol). Immediately, a white product separated. The reaction bulb was cooled with a salt/ice mixture, the product was sucked off by applying vacuum and washed with diethyl ether. The final product was dried in vacuo under cooling. Yield: 13.2 g (69%). No satisfactory elemental analysis results were obtained for $C_7H_{15}ClN_2Si$ because of the highly hygroscopic nature of the compound. ^{1}H NMR (CD_3CN): δ = 0.40 (s, 9 H, Si–Me_3), 3.68 (s, 3 H, C–Me), 6.87, 7.00, 7.59 (s, 3 H, imidazole–H) ppm. ^{13}C NMR (CD_3CN): δ = 3.3 (C–Si), 33.7 [C–Me (imidazole)], 120.6 [C (imidazole)], 129.2 [C (imidazole)], 138.3 [C (imidazole)] ppm. ^{29}Si NMR (CH_2Cl_2): δ = 30.1 ppm.

***N*-Methyl-*N*′-dimethyl(phenyl)silylimidazolium Chloride (4; MDMPhSIm-Cl):**[47] Prior to the synthesis, 1-methylimidazole (99%, Sigma Aldrich) and phenyldimethylchlorosilane (97%, ABCR) were freshly distilled. 1-Methylimidazole (12.55 mmol, 1.03 g) was placed in a Schlenk bulb, and an equimolar amount of phenyldimethylchlorosilane was slowly added whilst stirring. A white material precipitated, which was transferred into a glass ampoule for sublimation at 50 °C. ^{1}H NMR (300 MHz, CD_3CN): δ = 0.73 (s, 6 H, Me), 3.73 (s, 3 H, Me), 6.94–7.44 (s, 3 H, imidazole–H), 7.37–7.47 (m, 3 H, Ar–H), 7.66–7.68 (m, 2 H, Ar–H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 2.2 [C–(Si)], 33.9 [C (CH_3–imidazole)], 121.7 [C (imidazole)], 128.9 [C (imidazole)], 129.3 [Cm (Ar)], 131.6 [Cp (Ar)], 134.2 [Co (Ar)], 136.9 [C (imidazole)], 138.9 [C (Ar)] ppm.

Thermochemical Measurements

Vapour pressures and enthalpies of sublimation, $\Delta_{sub}H_m$, of the SILs MTMSIm-Br and BTMSIm-Br were determined by using the method of transpiration.[30] The temperature dependence of the vapour pressures was used to determine the enthalpies of sublimation of the pure substances. A sample of approximately 0.5 g was

mixed with glass beads and placed in a thermostatted U-tube of length 10 cm and diameter 0.5 cm. A stream of preheated nitrogen gas was passed through the U-tube at constant temperature (±0.1 K). The material transported was condensed in a cold trap. The amount of condensed product was determined by weight (±0.0001 g). The sublimation enthalpy was calculated from the temperature dependence of the vapour pressure at saturation (for details, see the Supporting Information).

Complementary to the method of transpiration, thermogravimetric analysis (TGA) was also used to measure the enthalpies of sublimation of the SILs. Both methods proved to be very efficient for measuring vaporization enthalpies of ILs with very low volatilities.[31] In this work, a Perkin–Elmer 6 TGA-device was used. With the Clausius–Clapeyron equation, the enthalpies of sublimation were obtained from the mass loss d*m*/d*t* (see the Supporting Information). In order to check for any changes in the substances during the measurements, ATR-IR measurements were performed. No change was observed in the spectra before and after the experiments, which indicates the intactness of the SIL samples. Furthermore, DSC measurements were performed before the measurements of the sublimation enthalpies, in order to detect any possible solid–solid phase transitions. A Mettler-Toledo-DSC-823 device was used. The measured data and further details are given in the Supporting Information.

Quantum Chemical Calculations

Standard first-principles electronic structure calculations were performed by using the Gaussian 03 Rev.04 program package.[48] Conformation analyses of the SILs were performed by using B3LYP/6-31+G(d,p) functionals with the help of a procedure developed in our previous work.[19] Optimized structures and the energy of the most stable conformer of the ion pairs were further obtained by using the CBS–QB3 composite method. CBS–QB3 theory uses geometries from the B3LYP/6-311G(2d,d,p) calculation and scaled zero-point energies from B3LYP/6-311G(2d,d,p) calculations followed by a series of single-point energy calculations at the MP2/6-311G(3df,2df,2p), MP4(SDQ)/6-31G(d(f),p) and CCSD(T)/6-31G† levels of theory.[36] Calculated values of the enthalpy of reaction are based on the electronic energy calculations obtained by using standard procedures of statistical thermodynamics.[49] Optimized gas-phase structures of the SILs, obtained by the CBS-QB3 theory, are shown in Figure 3.

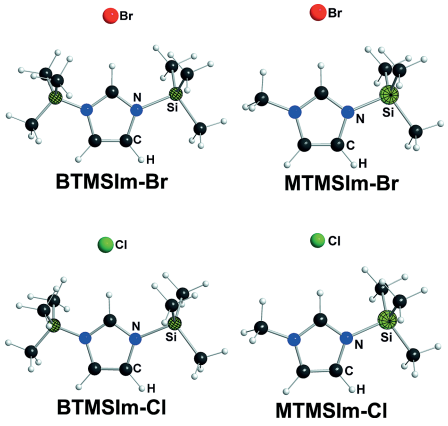

Figure 3. Gas-phase structures of the SILs, obtained by CBS–QB3 calculations.

NMR Measurements: ^{1}H-, ^{13}C- and ^{29}Si NMR spectra were recorded with a Bruker ARX 300 spectrometer. The spectra were calibrated with respect to the solvent signal (CD_3CN: ^{1}H δ = 1.93 ppm; ^{13}C δ = 1.3 ppm. $CDCl_3$: ^{1}H δ = 7.24 ppm; ^{13}C δ = 77.0 ppm).

Melting Points: Melting points (decomposition temperatures) were determined by DSC measurements with a Mettler Toledo DSC823e instrument in the range 0–200 °C with a heating rate of 10 K min^{-1} in an Ar atmosphere in a sealed Al crucible.

X-ray Crystallography: A suitable crystal of the title compound was mounted under inert conditions on a thin glass fibre using an inert oil. Diffraction measurements were performed with a Bruker-Nonius Apex X8 diffractometer having a CCD detector at 173 K. Graphite-monochromated Mo-K_α-radiation (λ = 0.71073 Å) was used. The raw data were corrected for Lorentz, polarization and absorption effects by using the Bruker-Nonius software.[50] The structures were solved by direct methods using SHELXS-97[51,52] and refined on F^2 by full-matrix least-squares techniques with the SHELXL-97[51,52] program. All H atoms of the title compounds were added on idealized positions and refined by using riding models. Crystal data, data collection and refinement parameters are summarized in Table 6.

CCDC-8972348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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